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THE EARTH SYSTEM***

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Radiation Entropy Flux and Entropy Production of the Earth System

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Abstract

Earth's radiation entropy flux at the top of the atmosphere (TOA) is reviewed with an emphasis on its estimation methods. Existing expressions for estimating radiation entropy flux are presented and their applicabilities are examined. The Earth's net TOA radiation entropy fluxes from different expressions differ substantially, larger than the typical entropy generation term associated with the atmospheric latent heat process. Using radiant energy flux over an absolute temperature underestimates the Earth's radiation entropy flux by >30%. The large difference in the Earth's reflected TOA solar radiation entropy flux from different expressions arises from their different assumptions on the Earth's reflection. For a graybody Earth with the Earth's albedo 0.30 and emissivity [0.50, 1.00], the magnitude of the Earth's net TOA radiation entropy flux from Planck's spectral expression ranges from 1.272 to 1.284 W m⁻² K⁻¹, equivalent to the overall Earth's entropy production rate of 6.481x10¹⁴ to 6.547x10¹⁴ W K⁻¹.

1. Introduction

The Earth system absorbs shortwave (SW) radiation energy from the Sun and degrades it into energy at lower terrestrial temperatures through various irreversible processes. Under steady-state assumption, the absorbed solar energy is re-radiated back to space in the form of longwave (LW) radiation. However, the entropy of the incoming SW radiation is much smaller than that of the outgoing LW radiation. The resulting negative entropy flux from the exchange of TOA radiations provides an estimate of the entropy exchange between the Earth and space and the potential Earth's entropy production [e.g., *Stephens and O'Brien*, 1993]. As a determinant source and sink of the Earth's energy and entropy, the radiation processes play a vital role in driving global circulations and shaping the Earth's climate.

Most studies on the Earth and its climate are based on the principles of energy, momentum and mass balances. The commonly accepted method is to use these principles to construct Earth-climate models (such as Atmosphere-Ocean General Circulation Models, or so called AOGCMs) to simulate various natural phenomena under investigation within the system. These models have made great contributions to developing climate theories and to making important decisions such as constraining greenhouse gas emission to avoid disastrous global climate change [e.g., IPCC, 2007]. However, because of the complexity of the Earth system, modern sophisticated models such as AOGCMs consider increasingly detailed processes with a large number of adjustable parameters embedded. These model parameters are often tuned to make good agreement between simulated results and observations. Recent studies indicate that the practice of tuning model parameters from model to model can lead to significant inconsistencies of the model bases, causing difficulty to accept and/or to understand their obtained results [e.g., *Cess et al.*, 1989; *Schwartz et al.*, 2007; *Kiehl*, 2007; a comment by *Kerr*, 2007]. Simple climate models with a few

parameters such as energy-balance models [e.g. *Frame et al.*, 2005; *Hegerl et al.*, 2006; *Wu and North*, 2007; see *North et al.*, 1981 for a review] and radiative-convective models [e.g., *Pauluis and Held*, 2002a,b; *Held et al.*, 2007; *Takahashi*, 2008; see *Ramanathan and Coakley*, 1978 for a review] have also been widely used for investigating global climate variations [e.g., *Manabe and Wetherald*, 1967; *Cess*, 1974; *North et al.*, 1983; *Betts and Ridgway*, 1989; *Kim and North*, 1991; *Weaver and Ramanathan*, 1995; *Pujol and North*, 2003]. Although those simple models have abilities to successfully simulate basic climate phenomena with no need of tuning a large number of model parameters, their limitations are obvious due to high simplification of detailed physical processes.

Another approach for studying the Earth's climate is to seek macroscopic principles that govern the climate system based on the second law of thermodynamics. As basic components of the second law of thermodynamics, entropy and entropy productions are fundamental to the thermodynamic approach of studying the Earth and its climate. Unlike the mainstream AOGCMs, entropy-based thermodynamic approaches do not need to consider detailed physical processes within the system. Although such an approach has not yet been developed as well as the theories of energy and mass balance, its applications have provided crucial insights into various processes of climatic importance in the past a few decades [e.g., *Paltridge* 1975, 1978; *Golitsyn and Mokhov*, 1978; *Nicolis and Nicolis*, 1980; *Grassl*, 1981; *Mobbs*, 1982; *Noda and Tokioka*, 1983; *Essex*, 1984, 1987; *Wyant*, 1988; *Lesins*, 1990; *Peixoco et al.*, 1991; *Stephens and O'Brien*, 1993; *Goody and Abdou*, 1996; *Goody*, 2000; *Ozawa et al.*, 2003]. For the Earth system at a steady-state, its incoming and outgoing radiation energy is balanced to each other while the outgoing radiation entropy is much larger than the incoming radiation entropy because of the large difference between the effective emissive temperatures of the solar and Earth

systems. The net entropy flux from the exchange of TOA radiations is balanced by the Earth's entropy production rate [e.g., *Stephens and O'Brien*, 1993]. As a key property of the Earth system, the Earth's entropy production rate measures the overall strength of all the processes involved, including the global circulation, and provides an important macroscopic constraint on the Earth system.

Although many efforts have been devoted to calculate the Earth's entropy production rate through the Earth's TOA radiation entropy fluxes, the expressions for calculating the Earth's TOA radiation entropy fluxes used in previous studies differ substantially. Some researches simply use a radiant energy flux divided by an absolute temperature [e.g., *Noda and Tokioka*, 1983; *Peixoco et al.*, 1991; *Ozawa et al.*, 2003]. Others give the radiation entropy flux by making analogy to Planck's expression for blackbody radiation entropy flux [Eq. (13) below] [e.g., *Peleta* 1961, 1964, 2003], or employ Planck's expression for spectral radiation entropy flux [Eq. (2) below] [e.g., *Aoki*, 1983; *Essex*, 1984; *Lesins*, 1990; *Stephens and O'Brien*, 1993; *Hold and Essex*, 1997]. The values of the Earth's TOA radiation entropy fluxes from the different expressions can be far from each other [e.g., *Noda and Tokioka*, 1983; *Stephens and O'Brien*, 1993; *Peixoco et al.*, 1991; *Ozawa et al.*, 2003]. The inconsistency in estimating the Earth's TOA radiation entropy fluxes causes confusion in understanding the thermodynamics of the Earth system inferred from these different estimates. Furthermore, the expressions for calculating radiation entropy flux have been developed and scattered in different fields for different purposes (such as engineering and Earth science). There is thus a need to survey the existing expressions and to clarify their applicabilities in calculating radiation entropy fluxes.

In this paper, we first review Planck's radiation theory (section 2), and present various existing expressions for calculating radiation entropy flux and analyze the assumptions

underlying these expressions (section 3). Then we construct several expressions for calculating the Earth's TOA radiation entropy fluxes under a graybody Earth's assumption (section 4). According to these constructed expressions, we calculate and compare the magnitudes of the Earth's TOA radiation entropy fluxes (section 5). Relative errors or differences to those directly calculated from Planck's expression for the spectral radiation entropy flux [Eq. (2) below] are presented and their possible causes are demonstrated (section 5). Physics underlying the expressions for calculating the Earth's reflected TOA SW radiation entropy flux are demonstrated (section 6). The final section (section 7) provides concluding remarks from this study. Note that, a brief introduction of calculating radiation entropy fluxes of a graybody planet in radiative equilibrium is provided in Appendix A based on Planck's radiation theory. A summary of notation is listed in Appendix B.

2. Basic concepts and Planck's theory of radiation entropy flux

Back in 1865 Rudolf Clausius defined the thermodynamic concept 'entropy' of a system as a summation of 'heat supplied' divided by its absolute 'temperature' [e.g., *Guggenheim* 1959; *Ozawa et al.*, 2003]. If a certain small amount of heat $d\tilde{Q}$ is supplied quasi-statically to a system with an absolute temperature T , the entropy S of the system will increase by $dS = d\tilde{Q}/T$. The Clausius entropy was proposed to study thermodynamic systems involving with material energy transfers, not with the radiation process that can propagate energy through electromagnetic waves in the absence of matter. Radiation travelling through empty space from the Sun to the Earth or to other planets in the solar system is a typical example of the latter.

An introduction of the concept of radiation entropy can be dated back to *Wien* [1894]. In his paper, Wien extended the terms temperature and entropy from a field of a material particle to

radiation in empty space and also defined a blackbody as an ideal body which completely absorbs all radiations [e.g., http://nobelprize.org/nobel_prizes/physics/laureates/1911/wien-bio.html]. *Planck* [1913] was the first to establish a firm theoretical foundation on radiation entropy, and derived theoretical expressions for the spectral entropy flux of a monochromatic radiation beam and the space entropy density for blackbody radiation in thermodynamic equilibrium. This section majorly introduces the main elements of Planck's theory on blackbody radiation entropy that are relevant to this paper.

Briefly, *Planck* [1913] derived the expressions of the spectral energy and entropy fluxes for a monochromatic radiation beam of frequency ν under thermodynamic equilibrium as

$$K_\nu = \frac{n_0 h \nu^3}{c^2} \left\{ \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \right\} \quad (1)$$

$$L_\nu = \frac{n_0 k \nu^2}{c^2} \left\{ \left(1 + \frac{c^2 K_\nu}{n_0 h \nu^3} \right) \ln \left(1 + \frac{c^2 K_\nu}{n_0 h \nu^3} \right) - \frac{c^2 K_\nu}{n_0 h \nu^3} \ln \frac{c^2 K_\nu}{n_0 h \nu^3} \right\} \quad (2)$$

where K_ν and L_ν are spectral energy and entropy fluxes per solid angle per frequency ν respectively; h , c and k are Planck's constant, speed of light in vacuum and Boltzmann constant respectively; T is the equilibrium temperature of a blackbody; n_0 denotes the state of polarization, with $n_0 = 1$ or 2 representing polarized or unpolarized rays respectively.

The derivation of Eq. (2) was based on the general connection between entropy and thermodynamic probability of a system and was called ‘mechanical expression’ of the spectral radiation entropy flux by Planck.

Based on Eqs. (1) and (2), the spectral space energy and entropy densities (u_ν and s_ν) for uniform monochromatic unpolarized radiation beams of frequency ν are expressed as

$$u_\nu = \frac{1}{c} \int K_\nu d\Omega = \frac{4\pi K_\nu}{c} = \frac{8\pi h\nu^3}{c^3} \left\{ \frac{1}{\exp\left(\frac{h\nu}{\kappa T}\right) - 1} \right\} \quad (3)$$

$$s_\nu = \frac{1}{c} \int L_\nu d\Omega = \frac{4\pi L_\nu}{c} = \frac{8\pi \kappa \nu^2}{c^3} \left\{ \left(1 + \frac{c^3 u_\nu}{8\pi h\nu^3}\right) \ln \left(1 + \frac{c^3 u_\nu}{8\pi h\nu^3}\right) - \frac{c^3 u_\nu}{8\pi h\nu^3} \ln \frac{c^3 u_\nu}{8\pi h\nu^3} \right\} \quad (4)$$

Integration of Eq. (3) over all frequencies leads to the space energy density of blackbody radiation as

$$u = 8\pi h c^{-3} \int_0^\infty \left\{ \exp\left(-\frac{h\nu}{\kappa T}\right) + \exp\left(-2\frac{h\nu}{\kappa T}\right) + \exp\left(-3\frac{h\nu}{\kappa T}\right) + \dots \right\} \nu^3 d\nu = aT^4 \quad (5)$$

where $a = 7.5737 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ is the radiation constant. A combination of Eqs. (3), (4) and (5) leads to

$$u = \int_0^\infty u_\nu d\nu = \frac{4\pi}{c} \int_0^\infty K_\nu d\nu = \frac{4\pi K}{c} = aT^4 \quad (6)$$

$$s = \int_0^\infty s_\nu d\nu = \frac{4\pi}{c} \int_0^\infty L_\nu d\nu = \frac{4\pi L}{c} \quad (7)$$

where u and s are space radiation energy and entropy densities; K and L are radiation energy and entropy fluxes per solid angle.

Based on Eqs. (5), (6) and (7), the expressions for the blackbody radiation energy and entropy fluxes (E and J) can be written as

$$E = \int K \cos\theta d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi/2} K \sin\theta \cos\theta d\theta = \pi K = \frac{ac}{4} T^4 = \sigma T^4 \quad (8)$$

$$J = \int L \cos\theta d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi/2} L \sin\theta \cos\theta d\theta = \pi L = \frac{c}{4} s \quad (9)$$

where θ and Ω are the zenith angle and solid angle of radiation beams, φ is azimuth angle.

In order to express the blackbody entropy flux as a function of known temperature T , *Planck* [1913] employed thermodynamic principles to derive the expressions of the entropy S and then the space entropy density s for a cavity V enclosing blackbody radiation with temperature T in thermodynamic equilibrium as (dU is the change of internal energy of a system)

$$S = \int dS = \int \frac{d\tilde{Q}}{T} = \int \frac{dU + pdV}{T} = \int \frac{udV + pdV}{T} = \int \frac{4}{3} aT^3 dV = \frac{4}{3} aT^3 V \quad (10)$$

$$s = \frac{S}{V} = \frac{4}{3} aT^3 \quad (11)$$

where p is the blackbody radiation pressure or so called Maxwell's radiation pressure with the same unit as pressure J m^{-3} , defined as a mechanical force exerted by electromagnetic radiation. The expression of p was derived in *Planck* [1913] for uniform radiation against any totally reflecting surface, that is,

$$p = \frac{u}{3} = \frac{a}{3} T^4 \quad (12)$$

Eq. (10) was called 'thermodynamic expression' of radiation entropy by Planck. By substituting Eq. (11) into Eq. (9), the blackbody radiation entropy flux J was obtained as a function of temperature T , that is,

$$J = \frac{c}{4} s = \frac{4}{3} \sigma T^3 = \frac{4}{3} \frac{E}{T} \quad (13)$$

So, for blackbody radiation under thermodynamic equilibrium, the 'mechanical expression' of the spectral radiation entropy flux [Eq. (2)] and the 'thermodynamic expression' of radiation entropy [Eq. (10)] had been reconciled into one simple expression of radiation entropy flux J as a

function of temperature T [Eq. (13)]. It indicates that the blackbody radiation entropy flux is equal to $4/3$ times its radiant energy flux divided by its effective radiative temperature. Note that the prefactor ‘ $4/3$ ’ stems from the entropy contribution from the blackbody radiation pressure.

It is noteworthy that a generalization of Planck’s spectral radiation entropy flux [Eq. (2)] into radiation of any type of polarization was made by *Rosen* [1954] through statistical definition of entropy (a measure of the randomness of a system through thermodynamic probability, see e.g., *Planck* [1913]). In contrast to *Rosen* [1954], *Ore* [1955] provided a comparative study of proving Eq. (2) as a general formulation in any radiation field. Both *Rosen* [1954] and *Ore* [1955] presented the statistical extension of the entropy concept to non-equilibrium states of a system. However, the temperature T in Eq. (1) for non-equilibrium radiation is frequency-dependent and should be defined as $T = \frac{\partial K_v}{\partial L_v}$ [e.g., *Ore*, 1955]. Later on, *Landsberg and Tonge* [1980] again proved the generalization of Eq. (2) for non-equilibrium radiation through the statistical definition of entropy. Therefore, for any thermal radiation with a known K_v , L_v can be calculated from Eq. (2) so that the radiation entropy flux J through a surface with a known zenith angle θ and a known solid angle Ω can be computed by

$$J = \int_0^\infty dv \int L_v \cos\theta d\Omega \quad (14)$$

For the sake of simplicity, the generalized expression of Planck’s spectral radiation entropy flux [Eq. (2)] will be referred to “Planck’s spectral expression” in the following context.

3. Existing expressions for non-blackbody radiation entropy flux

The Earth system is not a blackbody from the perspectives of both incoming and outgoing radiations. For example, the incoming solar radiation is partially absorbed, and partially reflected by various gases, aerosols and clouds in the atmosphere. The remainder reaches the Earth surface. The Earth's surface reflects a small part of the incoming solar radiation, absorbs the rest, warms up and then emits infrared radiation to the atmosphere. The atmosphere absorbs a part of the infrared radiation emitted by the Earth's surface (another part transmitted through the atmosphere), warms up and then re-emits infrared radiation both upwards (to outer space) and downwards (to the Earth's surface, so-called greenhouse warming). The atmospheric radiation absorption and transmission are basically determined by the atmospheric window, which depends on the properties of various atmospheric gases, aerosols and clouds. This makes atmospheric radiation absorption and transmission uneven in frequency band. In other words, the radiation property of the Earth system does not follow that of a blackbody. The non-blackbody property of the Earth system makes the calculations of the Earth's TOA radiation entropy fluxes much more challenging.

Furthermore, Planck's radiation theory indicates that blackbody radiation energy and entropy fluxes (E and J) exhibit a linear relationship [Eq. (13)] while the spectral radiation energy and entropy fluxes (K_v and L_v) are nonlinear to each other based on [Eq. (2)]. This nonlinearity makes it much more difficult to calculate a non-blackbody radiation entropy flux than that for a blackbody radiation entropy flux because the spectral radiation energy flux at all solid-angle elements over whole frequency band must be known before calculating a non-blackbody's radiation entropy flux. Over the last few decades, much attention has been devoted to developing approximate expressions for calculating non-blackbody radiation entropy flux in

different fields [e.g., *Rosen*, 1954; *Petela*, 1964; *Landsberg and Tonge*, 1979; *Stephens and O'Brien*, 1993; *Wright et al.*, 2001; *Liu and Chu*, 2006; *Wright*, 2007; *Zhang and Basu*, 2007].

The major existing expressions are summarized below.

In search for an approach to calculate the maximum ability of thermal radiation to perform work in a given environment (such as solar energy conversion), Peleta derived an expression for calculating radiation entropy flux of a ‘perfect’ graybody’s emission (a spectral distribution of energy emission conforming to Planck’s law [Eq. (1)], and emissivity ε independent of frequencies) in the 1960s [*Peleta*, 1961, 1964, 2003]. Briefly, the energy flux of such an ideal graybody radiation was given as

$$E = \varepsilon \sigma T^4 \quad (15)$$

By analogy to Planck’s theory of blackbody radiation energy and entropy fluxes, the expression of the corresponding radiation entropy flux was first given by Peleta [1961; 1964] as

$$J = \frac{4}{3} \varepsilon \sigma T^3 \quad (16)$$

Note that Eq. (16) is actually a result of substituting Eq. (15) into Eq. (13), which is an expression for blackbody radiation entropy flux. So, Eq. (16) represents only an approximation for calculating a graybody’s radiation entropy flux. Because of this analogy to blackbody radiation entropy flux, the resulting Eq. (16) suffers from major limitations for further applications.

In developing an accurate expression for calculating the efficiency of conversion of solar radiation into work (which is closely related to radiation energy and entropy fluxes), *Landsberg and Tonge* [1979] (hereafter referred to LT79) pointed out the limitations of Peleta's expression [Eq. (16)], and developed more accurate expressions for calculating radiation energy and entropy fluxes for a diluted blackbody (unpolarised) directly from Planck's spectral expression. The so-called diluted blackbody radiation considered in LT79 refers to the situation that the real photon number is the product of a dilution factor $\tilde{\epsilon}$ (≤ 1) and the photon number of the corresponding blackbody radiation (note that $\tilde{\epsilon}$ is independent of frequency in LT79). With this approximation, the spectral energy and entropy fluxes are given by

$$K_v(\tilde{\epsilon}) = \frac{2\tilde{\epsilon}h\nu^3}{c^2} \left\{ \frac{1}{\exp\left(\frac{h\nu}{\kappa T}\right) - 1} \right\} \quad (17)$$

$$L_v(\tilde{\epsilon}) = \frac{2\kappa\nu^2}{c^2} \left\{ \left(1 + \frac{c^2 K_v(\tilde{\epsilon})}{2h\nu^3} \right) \ln \left(1 + \frac{c^2 K_v(\tilde{\epsilon})}{2h\nu^3} \right) - \frac{c^2 K_v(\tilde{\epsilon})}{2h\nu^3} \ln \frac{c^2 K_v(\tilde{\epsilon})}{2h\nu^3} \right\} \quad (18)$$

Integrations of Eqs. (17) and (18) yield

$$E = \iint K_v(\tilde{\epsilon}) \cos\theta dv d\Omega = \frac{B\tilde{\epsilon}\sigma T^4}{\pi} \quad (19)$$

$$J = \iint L_v(\tilde{\epsilon}) \cos\theta dv d\Omega = \frac{\frac{4}{3}B\tilde{\epsilon}X(\tilde{\epsilon})\sigma T^3}{\pi} \quad (20a)$$

$$X(\tilde{\epsilon}) = \frac{45}{4} \pi^{-4} \tilde{\epsilon}^{-1} \int_0^{\infty} \beta^2 \left[\left(1 + \frac{\tilde{\epsilon}}{e^{\beta} - 1} \right) \ln \left(1 + \frac{\tilde{\epsilon}}{e^{\beta} - 1} \right) - \frac{\tilde{\epsilon}}{e^{\beta} - 1} \ln \frac{\tilde{\epsilon}}{e^{\beta} - 1} \right] d\beta \quad (20b)$$

where $\beta = hv/(kT)$; T is an ‘undiluted’ blackbody’s radiation temperature; $\sigma = 2\pi^5 k^4 / (15c^2 h^3)$ is the Stefan-Boltzmann constant, an introduction to the constant can be found in numerous references [e.g., *Guggenheim*, 1959 (section 13.05); *Landsberg*, 1961 (p274 for the details)]; over a hemisphere, the parameter $B = \int \cos\theta d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi/2} \sin\theta \cos\theta d\theta = \pi$. The dilution factor $\tilde{\epsilon}$ is equivalent to emissivity or absorptivity when applied to an isotropic emitter or absorber with constant emissivity or absorptivity. For $\tilde{\epsilon} < 0.10$, $X(\tilde{\epsilon})$ was simplified by LT79 as

$$X(\tilde{\epsilon}) \approx 0.9652 - 0.2777 \ln \tilde{\epsilon} + 0.0511 \tilde{\epsilon} \quad (21)$$

It was found by LT79 that $X(\tilde{\epsilon}) = 1$ when $\tilde{\epsilon} = 1$ (i.e., blackbody radiation), but $X(\tilde{\epsilon}) > 1$ when $\tilde{\epsilon} < 1$ (i.e., non-blackbody radiation). In other words, the expression of radiation entropy flux for an extreme case ($\tilde{\epsilon} = 1$, blackbody radiation) given by LT79 is the same as Peleta’s expression [Eq. (16)], and both are consistent to Planck’s expression for blackbody radiation entropy flux [Eq. (13)]. But, for a general case ($\tilde{\epsilon} < 1$, non-blackbody radiation), LT79 expression yields a radiation entropy flux larger than that from Peleta’s expression [Eq. (16)].

LT79 represents an important progress in understanding non-blackbody radiation entropy flux and developing an approximate expression for calculating non-blackbody radiation entropy flux. By following LT79’s step, *Stephens and O’Brien* [1993] (hereafter SO93) developed a similar approximate expression as LT79 and applied it into the calculation of the Earth’s

reflected TOA SW radiation entropy flux. By assuming a distant blackbody Sun illuminating a Lambertian spherical-geometrical surface of the Earth system (i.e., the reflected TOA SW radiation energy flux is the same in all direction and independent of the direction of incident solar radiation) with the Earth's albedo α_p independent of frequencies, SO93 arrived at their expression of the Earth's reflected TOA SW (hereafter marked as 'SR' in relevant expressions) radiation entropy flux as

$$\begin{aligned}
 J_{SR}^{SO93} &= \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left(1 + \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right) \ln \left(1 + \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right) - \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \ln \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right\} d\nu \\
 &= \frac{2\pi k^4}{c^2 h^3} T_{Sun}^3 \int_0^\infty \beta_{Sun}^2 \left\{ \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right. \\
 &\quad \left. - \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right\} d\beta_{Sun} \\
 &= \frac{4}{3} \sigma T_{Sun}^3 \chi(\delta_0)
 \end{aligned} \tag{22}$$

where $\delta_0 = \alpha_p \cos\theta_0 \frac{\Omega_0}{\pi}$; $\cos\theta_0$ is cosine of solar zenith angle to the Earth (estimated as a ratio of the Earth's TOA solar insolation and the solar constant 1367 W m^{-2} in analyzing the Earth's satellite measurements in SO93), the global averaged value of $\cos\theta_0$ is 0.25; Ω_0 is solar solid angle to the Earth $67.7 \times 10^{-6} \text{ sr}$; K_ν^{Sun} is the spectral energy flux of incident solar (SW) radiation per solid angle per frequency ν ; T_{Sun} is the Sun's emissive temperature 5779 K; $\beta_{Sun} = h\nu/(kT_{Sun})$. Similar to the case of the diluted blackbody radiation, the approximate expression of $\chi(\delta_0)$ was derived by SO93 for a small $\delta_0 (\ll 1)$ as

$$\begin{aligned}
\chi(\delta_0) &= \frac{45}{4\pi^4} \int_0^\infty \beta_{Sun}^2 \left\{ \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right. \\
&\quad \left. - \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right\} d\beta_{Sun} \\
&\approx \delta_0 (-0.27765652 \ln(\delta_0) + 0.96515744)
\end{aligned} \tag{23}$$

Clearly, the two approximate expressions Eq. (21) and Eq. (23) are similar to each other if

$\delta_0 = \tilde{\varepsilon}$. In other words, δ_0 (i.e., $\alpha_P \cos \theta_0 \frac{\Omega_0}{\pi}$) can be viewed as the dilution factor for the Earth's reflected TOA SW radiation if the Lambertian assumption is applied for the Earth system.

Besides, as a part of their developments, SO93 also provided a general expression for $\chi(\delta_0)$ that is valid for $0 \leq \delta_0 \leq 1$. Unfortunately, this general expression is too complicated to use in practice for calculating the radiation entropy flux.

Although LT79 expression Eq. (20a) and SO93 expression Eq.(22) are both derived directly from Planck's spectral expression, their applications are limited because their simplified approximate expressions were derived for small parameters $\tilde{\varepsilon}$ ($\tilde{\varepsilon} < 0.10$) or δ_0 ($\delta_0 \ll 1$). In order to develop a practical expression of radiation entropy flux effective for all values of emissivity ($0 \leq \varepsilon \leq 1$), *Wright et al.* [2001] (hereafter WSHR01) scrutinized Planck's 'mechanical expression' of spectral radiation entropy flux and derived an approximate expression for an isotropic graybody's radiation entropy flux with emissivity independent of frequencies. Based on Planck's spectral expression, the radiation entropy flux of such an isotropic graybody can be readily written as

$$\begin{aligned}
J^{GR} &= \int_0^\infty \frac{2\pi\kappa v^2}{c^2} \left\{ \left(1 + \frac{c^2 \varepsilon K_v}{2h v^3} \right) \ln \left(1 + \frac{c^2 \varepsilon K_v}{2h v^3} \right) - \frac{c^2 \varepsilon K_v}{2h v^3} \ln \frac{c^2 \varepsilon K_v}{2h v^3} \right\} dv \\
&= \frac{2\pi k^4}{c^2 h^3} T^3 \int_0^\infty \beta^2 \left\{ \left(1 + \frac{\varepsilon}{e^\beta - 1} \right) \ln \left(1 + \frac{\varepsilon}{e^\beta - 1} \right) - \left(\frac{\varepsilon}{e^\beta - 1} \right) \ln \left(\frac{\varepsilon}{e^\beta - 1} \right) \right\} d\beta \\
&= \frac{2\pi k^4}{c^2 h^3} T^3 I(\varepsilon) = \frac{2\pi k^4}{c^2 h^3} T^3 \left(\frac{4\pi^4}{45} \chi(\varepsilon) \right)
\end{aligned} \tag{24}$$

An approximate expression of function $I(\varepsilon)$ was derived by WSHR01 as

$$\hat{I}(\varepsilon) = \varepsilon \left\{ \frac{4\pi^4}{45} - m \ln \varepsilon \right\} \tag{25}$$

where $m = c_1$ or $m = c_2 - c_3 \varepsilon$ with constant parameters c_1 , c_2 and c_3 . The percentage errors caused by Eq. (25) were found less than 1.9% over $0 \leq \varepsilon \leq 1$ and the least accuracy occurs when ε is close to zero. The maximum percent errors caused by Eq. (25) in calculating radiation entropy flux from Eq. (24) for various emissivity ranges were shown in WSHR01's Table 2.

Along with the methodology advancement in calculating radiation entropy flux, *Zhang and Basu* [2007] investigated entropy flow and generation when incoherent multiple reflections are included. In their study, they re-examined the potential errors existed in Peleta's expression of radiation entropy flux [Eq. (16)] for a case of graybody emission only. They found that Peleta's expression always underestimates the radiation entropy flux directly calculated from Planck's spectral expression (see Fig 2 in *Zhang and Basu* [2007]). However, the relative errors tend to zero when emissivity approaches to 1.0 (i.e., blackbody). Apart from this, for a graybody

emission and a blackbody emission with the same total emissive energy flux, the peaks of the blackbody and graybody spectral emissive energy fluxes were found at different frequencies (see Fig3a in *Zhang and Basu* [2007]). The two emissive energy flux curves only crossover at some particular frequency, which means that the graybody's radiation temperature only at that frequency is equal to the blackbody's radiation temperature. This implies that a graybody radiation temperature is indeed frequency dependent (see Fig. 4 in *Zhang and Basu* [2007]). This fact was noticed earlier by *Landsberg and Tonge* [1979]. This indicates that it is not suitable for calculating a graybody's radiation entropy flux by setting an equivalent blackbody with the same emissive energy flux. Moreover, for a given emissive temperature, the estimated radiation entropy flux from Bejan's expression ($L_v = 4K_v/(3T_v)$) [*Bejan*, 1997] was demonstrated to overestimate or underestimate that from Planck's spectral expression at different frequencies (see Fig3b in *Zhang and Basu* [2007]).

The expression of radiant energy flux over an absolute temperature was also used for calculating radiation entropy flux in some publications [e.g., *Noda and Tokioka*, 1983; *Peixoco et al.*, 1991; *Ozawa et al.*, 2003]. However, several other publications emphasized that this expression cannot account for radiation entropy flux [e.g., *Essex*, 1984; *Stephens and O'Brien*, 1993; *Liu and Chu*, 2006; *Wright*, 2001, 2007]. For example, *Liu and Chu* [2006] presented three examples about the entropy generation formula of radiation energy transfer processes to conclude that the formula dQ/T of entropy generation rate generally cannot be used to calculate the local entropy generation rate of radiation energy transfer. In order to figure out a simple way to calculate the net radiation entropy flux considering the different combinations of incident, reflected and emitted radiations, *Wright* [2007] derived a so-called 'entropy coefficient' expression of the net radiation entropy flux, which is the ratio of the net entropy flux by the

combination of incident, reflected and emitted radiations to the entropy flux by the net radiant energy flux divided by an absolute temperature dQ/T . He found that the expression dQ/T can either underestimate or overestimate the net radiation entropy flux, depending on the temperatures of incident and emitted radiations.

4. Expressions for calculating the Earth's TOA radiation entropy fluxes

Based on the existing expressions developed for calculating radiation entropy flux, several expressions are constructed here for calculating the Earth's TOA radiation entropy fluxes. We assume that the blackbody Sun illuminates a spherical graybody Earth system. The Earth system absorbs 70% incident solar (SW) radiation (after reflecting 30%), warms up and then in turn emits terrestrial (LW) radiation to space. This irreversible radiative-transfer process is assumed to satisfy radiative energy equilibrium. A simple illustration of calculating a graybody planet's incoming/reflecting SW and outgoing LW radiation entropy fluxes based on Planck's radiation theory is provided in Appendix A.

We assume that the Earth system has a longwave emissivity ε_p (with respect to the Earth's effective emissive temperature T_p) and shortwave albedo α_p , both independent of frequencies. The Earth's TOA SW radiation entropy flux from incident solar radiation can be calculated by $(4/3)\sigma T_{Sun}^3 \cos\theta_0 \Omega_0 / \pi$. The global averaged cosine of solar zenith angle ($\cos\theta_0 = 0.25$) and solar solid angle ($\Omega_0 = 67.7 \times 10^{-6}$ sr) are used as in SO93. We retain the same Lambertian assumption for the Earth system as in SO93 as well. According to Planck's spectral expression, for such a graybody Earth system, we can get general expressions of the Earth's reflected TOA SW radiation entropy flux and the Earth's outgoing TOA LW radiation entropy flux as

$$\begin{aligned}
J_{SR}^{Planck} &= \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left(1 + \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right) \ln \left(1 + \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right) - \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \ln \frac{c^2\delta_0 K_\nu^{Sun}}{2h\nu^3} \right\} d\nu \\
&= \frac{2\pi k^4}{c^2 h^3} T_{Sun}^3 \int_0^\infty \beta_{Sun}^2 \left\{ \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(1 + \frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right. \\
&\quad \left. - \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \ln \left(\frac{\delta_0}{e^{\beta_{Sun}} - 1} \right) \right\} d\beta_{Sun}
\end{aligned} \tag{26}$$

$$\begin{aligned}
J_{LW}^{Planck} &= \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left(1 + \frac{c^2\varepsilon_P K_\nu^P}{2h\nu^3} \right) \ln \left(1 + \frac{c^2\varepsilon_P K_\nu^P}{2h\nu^3} \right) - \frac{c^2\varepsilon_P K_\nu^P}{2h\nu^3} \ln \frac{c^2\varepsilon_P K_\nu^P}{2h\nu^3} \right\} d\nu \\
&= \frac{2\pi k^4}{c^2 h^3} T_P^3 \int_0^\infty \beta_P^2 \left\{ \left(1 + \frac{\varepsilon_P}{e^{\beta_P} - 1} \right) \ln \left(1 + \frac{\varepsilon_P}{e^{\beta_P} - 1} \right) - \left(\frac{\varepsilon_P}{e^{\beta_P} - 1} \right) \ln \left(\frac{\varepsilon_P}{e^{\beta_P} - 1} \right) \right\} d\beta_P
\end{aligned} \tag{27}$$

where $\beta_{Sun} = h\nu/(kT_{Sun})$ and $\beta_P = h\nu/(kT_P)$, K_ν^P is the spectral energy flux of the Earth's TOA LW radiation per solid angle per frequency ν . If one knows the Earth's emissivity ε_P , the Earth's effective emissive temperature T_P can be determined by the hypothesis of TOA radiative energy equilibrium, i.e., $Q_0(1 - \alpha_P) = 4\varepsilon_P\sigma T_P^4$.

By employing the approximate expressions from *Peleta* [1964] (hereafter P64), LT79, SO93, WSHR01, we can get the simplified expressions of Eqs. (26) and (27) as

$$J_{SR}^{P64} = \frac{4}{3} \delta_0 \sigma T_{Sun}^3 \tag{28}$$

$$J_{SR}^{LT79} = \frac{8\pi^5 k^4}{45c^2 h^3} \delta_0 [-0.2777 \ln(\delta_0) + 0.9652 + 0.0511\delta_0] T_{Sun}^3 \quad (29)$$

$$J_{SR}^{SO93} = \frac{8\pi^5 k^4}{45c^2 h^3} \delta_0 [-0.27765652 \ln(\delta_0) + 0.96515744] T_{Sun}^3 \quad (30)$$

$$J_{SR}^{WSHR01} = \frac{2\pi k^4}{c^2 h^3} \delta_0 \left\{ \frac{4\pi^4}{45} - (2.336 - 0.260\delta_0) \ln \delta_0 \right\} T_{Sun}^3 \quad (31)$$

$$J_{LW}^{P64} = \frac{4}{3} \varepsilon_P \sigma T_P^3 \quad (32)$$

$$J_{LW}^{LT79} = \frac{8\pi^5 k^4}{45c^2 h^3} \varepsilon_P (-0.2777 \ln(\varepsilon_P) + 0.9652 + 0.0511\varepsilon_P) T_P^3 \quad (33)$$

$$J_{LW}^{SO93} = \frac{8\pi^5 k^4}{45c^2 h^3} \varepsilon_P (-0.27765652 \ln(\varepsilon_P) + 0.96515744) T_P^3 \quad (34)$$

$$J_{LW}^{WSHR01} = \frac{2\pi k^4}{c^2 h^3} \varepsilon_P \left\{ \frac{4\pi^4}{45} - (2.336 - 0.260\varepsilon_P) \ln \varepsilon_P \right\} T_P^3 \quad (35)$$

Note that, the maximum error of a graybody radiation entropy flux calculated from WSHR01's expression [Eqs. (24) and (25)] with $m = c_2 - c_3\varepsilon$ ($c_2 = 2.336$, $c_3 = 0.260$) was argued only 0.33% within emissivity range [0.005, 1.0] [Wright *et al.*, 2001], which is well satisfied by the present situation for the Earth system.

Using radiant energy flux divided by an effective emissive temperature (we mark this expression as 'M', means the expression satisfying for material energy transfer), the Earth's reflected TOA SW radiation entropy flux and the Earth's outgoing TOA LW radiation entropy flux can be written as

$$J_{SR}^M = \frac{Q_{SR}}{T_{Sun}} = \frac{\alpha_P Q_0}{4T_{Sun}} \quad (36)$$

$$J_{LW}^M = \frac{Q_{TOA}}{T_P} = \frac{(1 - \alpha_P)Q_0}{4T_P} \quad (37)$$

where Q_0 , Q_{SR} and Q_{TOA} are solar constant, the Earth's reflected TOA SW radiant energy flux $\alpha_P Q_0/4$ and the Earth's net TOA radiant energy flux $(1 - \alpha_P)Q_0/4$. The difference of the entropy fluxes between the incident solar radiation and the Earth's reflected TOA SW radiation determines the Earth's net TOA SW radiation entropy flux.

Similarly, by using the net TOA SW energy flux divided by the Sun's effective emissive temperature, the Earth's net TOA SW radiation entropy flux can be expressed as

$$J_{SW}^M = \frac{Q_{TOA}}{T_{Sun}} = \frac{(1 - \alpha_P)Q_0}{4T_{Sun}}$$

(38)

5. Comparison studies

The Earth's TOA LW and SW radiation entropy fluxes calculated from those expressions constructed in section 4 are compared and the errors relative to those directly calculated from Planck's spectral expression are analyzed in this section.

Figure 1 (a and b) shows the Earth's outgoing TOA LW radiation entropy flux from the different expressions for the case of the Earth's albedo 0.30, and the relative errors to those from Planck's spectral expression. The results from WSHR01, SO93 and LT79 expressions agree quite well with each other and also with those from Planck's spectral expression. The results from WSHR01 show the best agreement with those from Planck's spectral expression. The difference between SO93 and WSHR01 tends to increase when the emissivity approaches to 1.00 (i.e., blackbody). For large emissivity (say > 0.90), the relative errors [i.e., (WSHR01 minus SO93) over WSHR01] are within 3.12% to 3.48%. The results from WSHR01 and LT79 almost perfectly agree with those from Planck's spectral expression. When the emissivity approaches to 1.00, the result from SO93 [Eq. (34)] is not able to reconcile into that from Planck's expression of blackbody radiation entropy flux [Eq. (13)] $(4/3)\sigma T_P^3$ but $(4/3)\sigma T_P^3 \times 0.96515744$ instead. On the other hand, the results by P64 and Q_{TOA}/T_P [i.e., $(1 - \alpha_P)Q_0/(4T_P)$] clearly underestimate those from Planck's spectral expression, especially for lower emissivity values. The relative errors decrease when the emissivity increases (shown in Figure 1b). For emissivity > 0.50 , the relative errors from P64 are 0% - 15%, much smaller than those from Q_{TOA}/T_P (within

25% - 36%). Notice that, Figure 1 clearly show that the blackbody radiation entropy flux (i.e., emissivity equals 1.00) is equal to $4/3$ multiplying by Q_{TOA}/T_P . Obviously P64 expression is able to correctly calculate this extreme case.

Within the plausible range of the Earth's emissivity [0.50, 1.00] (i.e., the Earth's effective emissive temperature is lower than 303.08 K according to the hypothesis of TOA radiative energy equilibrium), the magnitude of the Earth's outgoing TOA LW radiation entropy flux from Planck's spectral expression ranges within 1.240 to 1.253 $\text{W m}^{-2} \text{K}^{-1}$. The magnitudes by WSHR01, SO93, LT79, P64 and Q_{TOA}/T_P are respectively in the ranges of 1.240 to 1.253 $\text{W m}^{-2} \text{K}^{-1}$, 1.209 to 1.220 $\text{W m}^{-2} \text{K}^{-1}$, 1.247 to 1.273 $\text{W m}^{-2} \text{K}^{-1}$, 1.052 to 1.252 $\text{W m}^{-2} \text{K}^{-1}$, and 0.789 to 0.939 $\text{W m}^{-2} \text{K}^{-1}$.

Figure 2 (a and b) shows the Earth's net TOA SW radiation entropy flux (the entropy flux from the Earth's reflected TOA SW radiation minus that from incident solar radiation, the positive represents outgoing entropy flux), and the differences relative to those from Planck's spectral expression. The results from Planck's spectral expression, WSHR01, SO93 and LT79 show significantly different patterns from others such as P64, Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$], and Q_{TOA}/T_{Sun} [i.e., $(1 - \alpha_P)Q_0/(4T_{Sun})$]. These results thus separate all the expressions into two groups. The majority of the former are positive while the latter are full of negative values. Results from WSHR01, SO93 and LT79 are very close to each other, and also agree with those from Planck's spectral expression. Note that, those from SO93 and LT79 agree the best with those from Planck's spectral expression, which implies good approximations of the expressions for a small parameter δ_0 . The results are also consistent with WSHR01's argument that the least accuracy of the WSHR01 expression occurs when its parameter (here the parameter is δ_0) is close to zero (reviewed in section 3).

The magnitude of the Earth's net TOA SW radiation entropy flux from Planck's spectral expression is $0.032 \text{ W m}^{-2} \text{ K}^{-1}$ for the Earth's albedo 0.30. The relative errors from WSHR01, SO93 and LT79 are small (5.2%, 0.3% and 0.25% respectively). P64 and Q_{SR}/T_{Sun} expressions always underestimate those from Planck's spectral expression, with the Earth's net TOA SW radiation entropy flux being -0.055 and $-0.061 \text{ W m}^{-2} \text{ K}^{-1}$ respectively for the case of the Earth's albedo 0.30. Note that the results from Q_{TOA}/T_{Sun} can overestimate or underestimate those from Planck's spectral expression in different albedo ranges. For the case of the Earth's albedo 0.30, the Earth's net TOA SW radiation entropy flux from Q_{TOA}/T_{Sun} ($-0.0414 \text{ W m}^{-2} \text{ K}^{-1}$) is almost identical to the value $-0.0413 \text{ W m}^{-2} \text{ K}^{-1}$ by *Peixoto et al.* [1991], where Q_{TOA} 238 W m^{-2} and T_{Sun} 5760K were used for calculating Q_{TOA}/T_{Sun} .

It is noteworthy that the magnitude of the Earth's net TOA SW radiation entropy flux from Planck's spectral expression $0.032 \text{ W m}^{-2} \text{ K}^{-1}$ is almost 40 times smaller than that of the Earth's TOA LW radiation entropy flux, which indicates that the Earth's outgoing LW radiation entropy flux dominates the Earth's net radiation entropy flux across the TOA and therefore the Earth's overall entropy production rate.

Figure 3a shows the Earth's net TOA radiation entropy flux. As expected, the characteristics of the Earth's net TOA radiation entropy flux are similar to those of the Earth's TOA LW radiation entropy flux shown in Figure 1a because of the dominant property of the Earth's TOA LW radiation entropy flux in all the Earth's TOA radiation entropy fluxes. Over the range of the Earth's emissivity [0.50, 1.00], the magnitude of the Earth's net TOA radiation entropy flux from Planck's spectral expression spans from 1.272 to $1.284 \text{ W m}^{-2} \text{ K}^{-1}$. The corresponding Earth's entropy production rate ranges from 6.481×10^{14} to $6.547 \times 10^{14} \text{ W K}^{-1}$. These results are very close to the global averaged values obtained by SO93 from the ERBE

measurement analysis (an average Earth's entropy production rate $6.8 \times 10^{14} \text{ W K}^{-1}$), where the Planck's expression of blackbody radiation entropy flux [Eq. (13)] was used to calculate the Earth's TOA incident solar radiation entropy flux and the Earth's TOA LW radiation entropy flux, and Lambertian assumption was used in calculating the Earth's reflected TOA SW radiation entropy flux. These results are also close to the Earth's entropy production rate $6 \times 10^{14} \text{ W K}^{-1}$ obtained by *Essex* [1984] as well, where the Planck's expression of blackbody radiation entropy flux [Eq. (13)] was used to calculate the TOA SW radiation entropy flux and the TOA LW radiation entropy flux (without separately calculating the reflected TOA SW radiation entropy flux), the effective emissive temperatures of the Sun and the Earth were assumed 5500 K and 250 K, and the TOA SW radiation was assumed converging in cones with vertices at the Earth subtending 0.5° . The results from WSHR01, SO93 and LT79 for the Earth's emissivity range [0.50, 1.00] are 1.270 to 1.283 $\text{W m}^{-2} \text{ K}^{-1}$, 1.241 to 1.251 $\text{W m}^{-2} \text{ K}^{-1}$ and 1.278 to 1.305 $\text{W m}^{-2} \text{ K}^{-1}$, respectively. The errors from WSHR01, SO93 and LT79 relative to those from Planck's spectral expression are ignorable, within 0.13% to 0.19%, within 1.64% to 3.41% and within 0.48% to 1.58%, respectively (shown in Figure 3b).

The Earth's net TOA radiation entropy flux from $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ [i.e., $(1 - \alpha_P)Q_0/(4T_P) - (1 - \alpha_P)Q_0/(4T_{Sun})$] is much different from that directly calculated from Planck's spectral expression (Figure 3a). The former is within [0.748, 0.897] $\text{W m}^{-2} \text{ K}^{-1}$ for the Earth's emissivity range [0.50, 1.00], much less than the latter. The relative errors of the former are as large as 30% to 41% (Figure 3b). These values, however, are very close to the Earth's net TOA radiation entropy flux 0.884 $\text{W m}^{-2} \text{ K}^{-1}$ by *Peixoto et al.* [1991], which was calculated from the expression dQ/T to evaluate the Earth's TOA radiation entropy fluxes from incident solar radiation energy flux and three parts of the Earth's outgoing LW radiation energy fluxes

(emissions by atmosphere, clouds and the Earth's surface). The Earth's net TOA radiation entropy flux from $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ are also close to $0.90 \text{ W m}^{-2} \text{ K}^{-1}$ by *Ozawa et al.* [2003], which was calculated from the expression $(Q_{TOA}/T_a - Q_{TOA}/T_{Sun})$ (T_a is a brightness temperature of the Earth's atmosphere) and using an observed global mean energy flux 240 W m^{-2} as the Earth's net TOA radiant energy flux, under assumptions of brightness temperatures of solar radiation T_{Sun} 5800 K and of the Earth's atmosphere T_a 255 K. The Earth's net TOA radiation entropy flux by using Q_{TOA}/T_P and Q_{SR}/T_{Sun} (i.e., separately calculate the reflected TOA SW radiation entropy flux) is close to that from $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$. The latter shows a slightly smaller error to that from Planck's spectral expression.

In addition, the accuracy of P64 expression increases when emissivity increases (Figure 3a). The magnitude of the Earth's net TOA radiation entropy flux from P64 ranges from 0.997 to $1.197 \text{ W m}^{-2} \text{ K}^{-1}$ for the Earth's emissivity range [0.50, 1.00]. The relative errors from P64 to those from Planck's spectral expression are within 7% - 22%. The Earth's net TOA radiation entropy flux from P64 is close to $1.187 \text{ W m}^{-2} \text{ K}^{-1}$ by *Aoki* [1983], where Planck's expression of blackbody radiation entropy flux [Eq. (13)] was used to calculate the Earth's incoming SW radiation entropy flux and the Earth's LW emission entropy flux without separately calculating the reflected solar radiation entropy flux (after calculating the net amount of the Earth's radiation entropy from absorbed SW radiation and emitted LW radiation, globally averaging the net Earth's radiation entropy to get the net Earth's radiation entropy flux $1.187 \text{ W m}^{-2} \text{ K}^{-1}$). The Earth's net TOA radiation entropy flux from P64 is also close to $1.204 \text{ W m}^{-2} \text{ K}^{-1}$ by *Weiss* [1996], where Planck's expression of blackbody radiation entropy flux [Eq. (13)] was used to calculate the entropy fluxes of the Earth's absorbed solar radiation and outgoing LW radiation (the Earth's net radiation energy flux used for calculating the Earth's net radiation entropy flux

was obtained by multiplying the solar constant with the Earth's coalbedo 0.72 and then performing a global average). A similar value 600 TW K^{-1} (equivalent to $1.174 \text{ W m}^{-2} \text{ K}^{-1}$ if using the Earth's radius 6378 km) was obtained by *Fortak* [1979] as well, where Planck's expression of blackbody radiation entropy flux [Eq. (13)] was used to calculate the Earth's net SW and outgoing LW radiation entropy fluxes (using solar radiant energy 17344 TW, the Sun's radiation temperature 5770 K, the radiation temperature of the Earth-atmosphere system 257 K, and the Earth's albedo 0.30).

The Earth's TOA radiation entropy fluxes for other values of the Earth's albedo from 0.00 to 1.00 are also examined in this study. The results present similar patterns to the one shown here, and thus omitted.

6. Physics underlying different expressions for calculating the Earth's reflected TOA SW radiation entropy flux

There is a puzzle in the Earth's net TOA SW radiation entropy flux calculated from the different expressions as shown in Figure 2. The Earth's net TOA SW radiation entropy fluxes from different expressions show opposite signs for most of the Earth's albedo values. Note that the entropy flux of the incident solar radiation is the same for all the cases, so the opposite signs of the Earth's net TOA SW radiation entropy flux are attributed to the expressions used to calculate the Earth's reflected TOA SW radiation entropy flux. Moreover, the difference between the Earth's reflected TOA SW radiation entropy flux from Planck's spectral expression and that from P64 for the extreme case ($\alpha_p = 1$) is difficult to understand. According to the properties of the two expressions, P64 should reconcile to Planck's spectral expression for the extreme cases ($\alpha_p = 0$ or 1) as discussed in our preceding sections and in *Zhang and Basu* [2007]. So, there

must be some fundamental difference in those expressions of calculating the Earth's reflected TOA SW radiation entropy flux.

The preceding calculations of the Earth's reflected TOA SW radiation entropy flux [Eq. (26)] is under the Lambertian assumption for the Earth's reflection (i.e., involving penetration into material and backscattering by its molecules or particles). This assumption indicates that the spectral energy flux of the Earth's reflected TOA SW radiation ($\alpha_P K_v^{Sun}$) is the same in all directions and independent of the incident direction (i.e., the same for solar zenith angle from 0 to $\pi/2$ in the illuminating hemisphere). Under this assumption, the spectral energy flux of the Earth's reflected TOA SW radiation equals

$$K_v = \frac{\alpha_P \cos \theta_0 \Omega_0}{\pi} K_v^{Sun} \quad (39)$$

Notice that the global averaged value of cosine of solar zenith angle $\cos \theta_0 (=0.25)$ is used here. By integrating Eq. (39) over all the frequency bands for the spherical Earth system, one can get the Earth's reflected TOA SW radiation energy flux $\int dv \int_0^{2\pi} d\varphi \int_0^{\pi/2} K_v \sin \theta \cos \theta d\theta = \alpha_P \cos \theta_0 \Omega_0 \int K_v^{Sun} dv$.

Now suppose that the Earth's reflection for the incident solar radiation is specular (i.e., mirror-like, following Fresnel's law) instead of diffusive (Lambertian surface is an idealized surface of diffusive reflection), the spectral energy flux of the Earth's reflected TOA SW radiation should be equal to the Earth's albedo α_P times that of the incident TOA SW radiation, i.e.,

$$K_v = \alpha_p K_v^{Sun} \quad (40)$$

Then the Earth's reflected TOA SW radiation energy flux [after integrating Eq. (40) in an effective range of the solid angle Ω_0 of the reflected solar beams and over all frequency bands] leads to $\int dv \int_{\Omega_0} K_v \cos\theta d\Omega = \alpha_p \int dv \int_{\Omega_0} K_v^{Sun} \cos\theta d\Omega = \alpha_p \cos\theta_0 \Omega_0 \int K_v^{Sun} dv$, which is identical to the Lambertian case. However, the physical meaning underlying Eq. (39) or Eq. (40) are totally different. The former's spectral energy flux per solid angle per frequency is averaged over a Lambertian Earth's surface while the latter's spectral energy flux per solid angle per frequency is only for the effective solid angle Ω_0 (i.e., under an assumption that the Earth's reflection to the incident solar radiation is specular).

If we use the expression of spectral energy flux of specular reflection [Eq. (40)] instead of that of diffusive reflection [Eq. (39)], the Earth's reflected TOA SW radiation entropy flux can be calculated by

$$J_{SR}^{Planck_new} = \frac{2\pi k^4}{c^2 h^3} T_{Sun}^3 \delta_1 \int_0^\infty \beta_{Sun}^2 \left\{ \left(1 + \frac{\alpha_p}{e^{\beta_{Sun}} - 1} \right) \ln \left(1 + \frac{\alpha_p}{e^{\beta_{Sun}} - 1} \right) - \left(\frac{\alpha_p}{e^{\beta_{Sun}} - 1} \right) \ln \left(\frac{\alpha_p}{e^{\beta_{Sun}} - 1} \right) \right\} d\beta_{Sun} \quad (41)$$

where $\delta_1 = \cos\theta_0 \Omega_0 / \pi$. By employing the approximate expressions developed by LT79, SO93 and WSHR01, Eq. (41) can be further simplified as

$$J_{SR}^{LT79_new} = \frac{8\pi^5 k^4}{45c^2 h^3} \delta_0 [-0.2777 \ln(\alpha_p) + 0.9652 + 0.0511\alpha_p] T_{Sun}^3 \quad (42)$$

$$J_{SR}^{SO93_new} = \frac{8\pi^5 k^4}{45c^2 h^3} \delta_0 [-0.27765652 \ln(\alpha_p) + 0.96515744] T_{Sun}^3 \quad (43)$$

$$J_{SR}^{WSHR01_new} = \frac{2\pi k^4}{c^2 h^3} \delta_0 \left\{ \frac{4\pi^4}{45} - (2.336 - 0.260\alpha_p) \ln \alpha_p \right\} T_{Sun}^3 \quad (44)$$

The obtained Earth's specular reflected TOA SW radiation entropy flux is shown in Figure 4. As expected, the results from WSHR01, SO93 and LT79 are very close to those from Planck's spectral expression. It can be clearly seen that the result from P64 reconciles to that from Planck's spectral expression when the Earth's albedo tends to 1. The one-third difference between the results from Q_{SR}/T_{Sun} [i.e., $\alpha_p Q_0/(4T_{Sun})$] and from Planck's spectral expression for the extreme case ($\alpha_p = 1$) can also be clearly seen in Figure 4.

According to our results, the calculations of the Earth's reflected TOA SW radiation entropy flux through P64 or Q_{SR}/T_{Sun} are identical to those under the assumption that the Earth's reflection to the incident solar radiation is specular. This assumption is not realistic for the Earth system because the Earth's reflection to the incident solar radiation is known to be diffusive, involving the processes of material penetration and various scattering through atmospheric gases, aerosols and clouds. It indicates that using P64 or the Earth's reflected TOA

SW radiant energy flux over the Sun's effective emissive temperature is not appropriate for calculating the Earth's reflected TOA SW radiation entropy flux.

Nevertheless, as for the accuracy of the Lambertian assumption in calculating the Earth's reflected TOA SW radiation entropy flux, SO93 provided a testing by employing a radiative-transfer model. SO93 showed that the Lambertian assumption leads to an overestimate of the Earth's reflected TOA SW radiation entropy flux by 20%, i.e., by multiplying an *ad hoc* factor 0.80 with the obtained Earth's reflected TOA SW radiation entropy flux under the Lambertian assumption can provide a good estimate. Although the Earth's specular reflection leads to an unrealistic Earth's reflected TOA SW radiation entropy flux $0.0310 \text{ W m}^{-2} \text{ K}^{-1}$, which is much smaller than $0.1102 \text{ W m}^{-2} \text{ K}^{-1}$ under the Lambertian assumption. These results imply that the real Earth's reflection may work between the Lambertian and specular reflections.

7. Concluding remarks

In this paper, we have reviewed basic concepts and Planck's theory about radiation entropy flux, as well as various existing expressions developed for calculating non-blackbody radiation entropy flux in different research fields. Expressions for calculating a graybody Earth's TOA radiation entropy fluxes are constructed based on those expressions for non-blackbody radiation. Errors of the obtained Earth's TOA radiation entropy fluxes from different expressions relative to those directly calculated from Planck's spectral expression are examined. The underlying physics existing in the different expressions are demonstrated as well.

The results of this study show that the differences of the Earth's TOA radiation entropy fluxes arising from different expressions are substantial. The Earth's net TOA radiation entropy flux from $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ shows large error ($> 30\%$, with the error's magnitude from

0.387 to 0.524 W m⁻² K⁻¹ corresponding to the Earth's emissivity range [0.5, 1.0]), compared to that from Planck's spectral expression. Based on the analysis by *Peixoto et al.* [1991], the largest entropy generation term of the Earth system is associated with atmospheric latent heat release and its magnitude is 0.298 W m⁻² K⁻¹. In other words, the difference of the Earth's net TOA radiation entropy flux arising from these different expressions can be tremendous, even greater than the largest entropy generation term of the Earth system.

As we reviewed in section 2, *Planck* [1913] explicitly pointed out the two kinds of expressions: 'mechanical expression' of spectral radiation entropy flux [Eq. (2)] and 'thermodynamic expression' of radiation entropy [Eq. (10)]. In Planck's cavity experiment [*Planck*, 1913], the 'heat supplied' term $d\tilde{Q}$ in 'thermodynamic expression' was detected to include two parts: emissive radiant energy (photon energy, $u dV$) and work done by radiation pressure ($p dV$). For blackbody radiation, its radiation pressure ('Maxwell's radiation pressure') has been explicitly derived by *Planck* [1913] so that the two entropy expressions had been reconciled into one simple expression of radiation entropy flux [Eq. (13)] (details in section 2). However, the situations are much more complicated for non-blackbody radiation including the determination of its radiation pressure and maybe some other factors associated with its entropy flux so that it is difficult to use the 'thermodynamic expression' for calculating radiation entropy flux. The significant underestimation by $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ is indeed (at least) associated with ignoring the radiation-pressure part in the 'heat supplied' term during the calculation. In other words, as long as Planck's theory [Eq. (2)] holds universality, the expression $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ does not include all individual radiation entropy contributions therefore cannot account for the overall TOA radiation entropy flux of the Earth system. In fact, the radiation pressures (i.e., a property associated with electromagnetic momentum, see e.g., *Crenshaw*

[2007]) of the Earth's TOA incoming SW and outgoing LW must be balanced to each other in order to satisfy the law of momentum conservation for the Earth system. The Earth's TOA radiation-pressure balance (i.e., no extra work done by the radiation pressure due to the incoming SW or the outgoing LW) is also consistent with the sense of TOA SW and LW radiative energy balance, which is commonly accepted worldwide for a steady-state Earth system.

The relative errors of the Earth's net TOA radiation entropy flux from P64 compared to those from Planck's expression are less than 7% - 22% for the Earth's emissivity range [0.50, 1.00]. The error decreases fast as the emissivity increases. As discussed in section 2, P64 comes actually from an analogy to blackbody radiation entropy flux. This expression can also be thought equivalent to Bejan's expression ($L_v = 4K_v/(3T_v)$) under assumptions of isotropic graybody Earth or isotropic reflected TOA SW radiation with the Earth's emissivity and albedo independent of frequencies. As discussed in section 3, Bejan's expression may cause errors in estimating radiation entropy flux, shown in Fig. 3b of *Zhang and Basu* [2007]. Anyway, the errors from P64 essentially arise from the expression's analogy to that of blackbody radiation. However, its errors are shown to be much less than those from $(Q_{TOA}/T_P - Q_{TOA}/T_{Sun})$ based on the results from this study.

The relative errors of the Earth's net TOA radiation entropy flux from WSHR01, SO93 or LT79 to those from Planck's spectral expression are ignorable, 0.13% to 0.19%, 1.64% to 3.41% or 0.48% to 1.58% respectively for the Earth's emissivity range [0.50, 1.00]. In other words, they are useful approximate expressions for calculating the Earth's TOA radiation entropy flux. By directly employing Planck's spectral expression, the magnitude of the Earth's net TOA radiation entropy flux ranges from 1.272 to 1.284 W m⁻² K⁻¹ (for the Earth's albedo 0.30 and emissivity range [0.50, 1.00]), the Earth's outgoing TOA LW radiation entropy flux ranges from 1.240 to

1.253 W m⁻² K⁻¹, and the Earth's net TOA SW radiation entropy flux equals a constant 0.032 W m⁻² K⁻¹. So, the equivalent Earth's entropy production rate ranges from 6.481x10¹⁴ to 6.547x10¹⁴ W K⁻¹. The Earth's outgoing TOA LW radiation entropy flux is obviously the predominant contributor for the overall Earth's entropy production rate.

The calculations of the Earth's reflected TOA SW radiation entropy flux from Planck's spectral expression and from P64 or Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$] are demonstrated having different physical bases. The former is based on the Lambertian assumption for the Earth's reflection to the incident solar radiation while the latter can be derived from the assumption that the Earth reflection is specular. Because the real Earth's reflection to incident solar radiation tends to more like a Lambertian (diffusive) than a specular (mirror-like), we recommend that the calculation of the Earth's reflected TOA SW radiation entropy flux should avoid using P64 or Q_{SR}/T_{Sun} .

This study tells us that caution must be taken in selecting approximate expressions for calculating the Earth's TOA radiation entropy fluxes in order to avoid large errors arisen from the calculating expressions. This study also shows that those expressions intrinsically derived from Planck's spectral expression, such as WSHR01, SO93 or LT79, are good expressions for calculating a graybody Earth's TOA radiation entropy fluxes. WSHR01 expression exhibits the best performance among all. It is noteworthy that the quantities of the Earth's TOA radiation entropy fluxes from this study are under some assumptions such as a graybody Earth and Lambertian Earth's surface. Although the expressions constructed in this study represent a useful extension from a blackbody Earth's assumption, the Earth system is clearly not a graybody neither. One may obtain the real values of the Earth's TOA radiation entropy fluxes through Planck's spectral expression or WSHR01/SO93/LT79 expressions if one can get all the

parameters needed in the expressions from modern advanced satellite measurements such as ERBE (Earth Radiation Budget Experiment) or CERES (Clouds and the Earth's Radiant Energy System). Quantifying the real Earth's TOA radiation entropy fluxes are obviously critical to the Earth's climate study. It will bring us a better understanding about the thermodynamic macroscopic constraint of the Earth system.

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Appendix A. Radiation Entropy Fluxes of a Graybody Planet in Radiative Equilibrium

This Appendix is aimed to provide introductive contents about the basic calculations of a spherical graybody planet's radiation entropy fluxes in radiative equilibrium in order to help those who are not familiar to this field.

A graybody planet can be thought as an idealized Earth system. We assume that the graybody planet is in radiative equilibrium with its planetary albedo $\alpha_P = 0.30$. Solar (SW) radiation impinges on the graybody planet, 30% reflected back to space and the rest absorbed by the planet. The planet warms up after receiving 70% incident SW radiation and radiates LW radiation to space. This simple process involves irreversible radiative energy transfer and so leads to the planet's entropy increase. The entropy exchange involved in this radiative energy transfer can be summarized into the following three aspects based on Planck's radiation theory:

1) The planet's entropy flux from the incident solar radiation $J_{SW}^{(in)}$ can be calculated based on Planck's expression of blackbody radiation entropy flux [Eq. (13)] and the global averaged cosine of solar zenith angle $\cos\theta_0$ and solar solid angle Ω_0 to the planet ($\cos\theta_0 = 0.25$ and $\Omega_0 = 67.7 \times 10^{-6}$ sr as those to the Earth), i.e.,

$$J_{SW}^{(in)} = \frac{4}{3} \sigma T_{Sun}^3 \frac{\int_{\Omega_0} \cos\theta d\Omega}{\int_0^{2\pi} d\varphi \int_0^{\pi/2} \sin\theta \cos\theta d\theta} = \frac{4}{3} \sigma T_{Sun}^3 \cos\theta_0 \frac{\Omega_0}{\pi} = 0.0786 \text{ W m}^{-2} \text{ K}^{-1}$$

where the Sun's effective emissive temperature T_{Sun} used here is 5779 K.

2) If the planet's reflection to the incident solar radiation obeys Lambertian assumption (i.e., the reflection is the same in all directions and independent of the direction of incident solar radiation), the planet's reflected SW spectral energy flux K_v equals $\alpha_P \cos\theta_0 \Omega_0 K_v^{Sun} / \pi$

(averaged over the Lambertian planet). So, the planet's entropy flux from the reflected SW radiation $J_{SW}^{(out)}$ under the Lambertian assumption can be calculated using Planck's spectral expression [Eq. (2)], i.e.,

$$J_{SW}^{(out)} = \int_0^\infty \frac{2\pi\kappa v^2}{c^2} \left\{ \left(1 + \frac{c^2 \delta_0 K_v^{Sun}}{2h v^3} \right) \ln \left(1 + \frac{c^2 \delta_0 K_v^{Sun}}{2h v^3} \right) - \frac{c^2 \delta_0 K_v^{Sun}}{2h v^3} \ln \frac{c^2 \delta_0 K_v^{Sun}}{2h v^3} \right\} dv$$

$$= 0.1102 \text{ W m}^{-2} \text{ K}^{-1}$$

where $\delta_0 = \alpha_p \cos \theta_0 \Omega_0 / \pi$ and $K_v^{Sun} = 2h v^3 / c^2 \{1 / [\exp(hv / (\kappa T_{Sun})) - 1]\}$, h , c and κ are Planck's constant, speed of light in vacuum and Boltzmann constant respectively, v is the frequency of a reflected radiation beam.

However, if we assume that the planet's reflection to the incident solar radiation is specular (mirror-like), the planet's reflected SW spectral energy flux K_v equals $\alpha_p K_v^{Sun}$ (only in an effective solar solid angle Ω_0 with solar zenith angle θ_0 to the planet). So, the planet's entropy flux from the reflected SW radiation $J_{SW}^{(out)}$ under the specular assumption can be calculated using Planck's spectral expression [Eq. (2)], i.e.,

$$J_{SW}^{(out)} = \int_0^\infty \frac{2\pi\kappa v^2 \delta_1}{c^2} \left\{ \left(1 + \frac{c^2 \alpha_p K_v^{Sun}}{2h v^3} \right) \ln \left(1 + \frac{c^2 \alpha_p K_v^{Sun}}{2h v^3} \right) - \frac{c^2 \alpha_p K_v^{Sun}}{2h v^3} \ln \frac{c^2 \alpha_p K_v^{Sun}}{2h v^3} \right\} dv$$

$$= 0.0310 \text{ W m}^{-2} \text{ K}^{-1}$$

where $\delta_1 = \cos \theta_0 \Omega_0 / \pi$.

3) The planet's entropy flux from its LW radiation emission $J_{LW}^{(out)}$ can be calculated based on Planck's spectral expression [Eq. (2)] and the planetary emissivity ε_p , i.e.,

$$J_{LW}^{(out)} = \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left(1 + \frac{c^2\varepsilon_P K_V^P}{2h\nu^3} \right) \ln \left(1 + \frac{c^2\varepsilon_P K_V^P}{2h\nu^3} \right) - \frac{c^2\varepsilon_P K_V^P}{2h\nu^3} \ln \frac{c^2\varepsilon_P K_V^P}{2h\nu^3} \right\} d\nu$$

where K_V^P is blackbody spectral energy flux of emissive temperature T_P , i.e., $K_V^P = 2h\nu^3 / c^2 \{1/[\exp(h\nu/(\kappa T_P)) - 1]\}$. For a given emissivity ε_P , T_P can be determined based on the planet's radiative-equilibrium assumption, i.e., the emitted LW radiation energy flux equals the absorbed SW radiation energy flux, $\pi R^2 Q_0 (1 - \alpha_P) = 4\pi R^2 \varepsilon_P \sigma T_P^4$, where Q_0 is the solar constant 1367 W m^{-2} , R is the planet's radius. For the planet's emissivity range $[0.50, 1.00]$ (i.e., the planet's effective emissive temperature is lower than 303.08 K), the planet's LW radiation entropy flux ranges from 1.2403 to $1.2529 \text{ W m}^{-2} \text{ K}^{-1}$. For the planet's emissivity range $[0.001, 0.50]$ (i.e., the planet's effective emissive temperature is higher than 303.08 K), the planet's LW radiation entropy flux ranges from 0.6423 to $1.2403 \text{ W m}^{-2} \text{ K}^{-1}$.

From the above three aspects of the planet's radiation entropy fluxes, the entropy exchange associated with the planet's LW emission and the planet's reflection to the SW radiation is much larger than that from the incident SW radiation. The overall increase of the planet's radiation entropy flux can be determined by $(J_{LW}^{(out)} + J_{SW}^{(out)} - J_{SW}^{(in)})$, which is balanced by the planet's total entropy production rate.

Note that, the maximum values of the net radiation entropy flux for various planets in radiative equilibrium as a function of albedo can be found in SO93 (Figure 12).

Appendix B. Summary of Notation

Glossary

a	radiation constant, $7.5737 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$
B	a geometrical factor in (19) and (20a), $B = \int \cos \theta d\Omega$, $B = \pi$ over a hemisphere
c	speed of light in vacuum, $2.9979 \times 10^8 \text{ m s}^{-1}$
c_1, c_2, c_3	constants for coefficient m in Eq. (25)
E	energy flux, W m^{-2}
E^{GR}	energy flux of graybody radiation, W m^{-2}
E_{SR}	energy flux of reflected solar radiation, W m^{-2}
h	Planck's constant, $6.626 \times 10^{-34} \text{ J s}$
$I(\varepsilon)$	a function of emissivity ε in Eq. (24)
$\hat{I}(\varepsilon)$	an approximate expression of the function $I(\varepsilon)$
J	entropy flux, $\text{W m}^{-2} \text{ K}^{-1}$
J^{GR}	entropy flux of gray-body radiation, $\text{W m}^{-2} \text{ K}^{-1}$
J_{SR}	entropy flux of reflected solar radiation, $\text{W m}^{-2} \text{ K}^{-1}$
J_{SW}	SW radiation entropy flux, $\text{W m}^{-2} \text{ K}^{-1}$
J_{LW}	LW radiation entropy flux, $\text{W m}^{-2} \text{ K}^{-1}$

K	energy flux per solid angle, $\text{W m}^{-2} \text{sr}^{-1}$
K_ν	spectral energy flux per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s}$
K_ν^P	spectral energy flux of a planet's TOA LW radiation per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s}$
K_ν^{Sun}	spectral energy flux of TOA incident solar (SW) radiation per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s}$
L	entropy flux per solid angle, $\text{W m}^{-2} \text{sr}^{-1} \text{K}^{-1}$
L_ν	spectral entropy flux per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$
L_ν^{GR}	spectral entropy flux of graybody radiation per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$
L_ν^{SR}	spectral entropy flux of reflected solar radiation per solid angle per frequency ν , $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$
m	a coefficient in Eq. (25)
n_0	state of polarization in Eqs. (1) and (2), $n_0 = 1$ or 2 for a polarized or unpolarized ray
p	radiation pressure, J m^{-3}
\tilde{Q}	heat, J
Q_0	solar constant, 1367 W m^{-2}

Q_{SR}	reflected TOA SW radiant energy flux ($\alpha_p Q_0/4$), W m^{-2}
Q_{TOA}	net TOA radiant energy flux $((1 - \alpha_p)Q_0/4)$, W m^{-2}
dQ	exchange of radiant energy flux, W m^{-2}
s	space entropy density, $\text{J m}^{-3} \text{K}^{-1}$
s_ν	spectral space entropy density per frequency ν , $\text{J m}^{-3} \text{K}^{-1} \text{s}$
S	entropy, J K^{-1}
T	temperature, K
T_P	a planet's effective emissive temperature, K
T_a	a brightness temperature of atmosphere in <i>Ozawa et al.</i> [2003], K
T_{Sun}	the Sun's emissive temperature, 5779 K
T_ν	temperature of monochromatic radiation beams at frequency ν , K
u	space energy density, J m^{-3}
u_ν	spectral space energy density per frequency ν , $\text{J m}^{-3} \text{s}$
U	internal energy of a system, J
V	volume, m^3
$X(\tilde{\epsilon})$	a function of the dilution factor $\tilde{\epsilon}$ in Eqs. (20a), (20b) and (21)

Greek symbols

α_P a planet's albedo

β non-dimensional group, $h\nu/(kT)$

β_P non-dimensional group, $h\nu/(kT_P)$

β_{Sun} non-dimensional group, $h\nu/(kT_{Sun})$

δ_0 non-dimensional group, $\alpha_P \cos\theta_0 \Omega_0/\pi$

δ_1 non-dimensional group, $\cos\theta_0 \Omega_0/\pi$

ε emissivity

ε_P a planet's emissivity

$\tilde{\varepsilon}$ a diluted factor, i.e., the photon number of diluted unpolarised blackbody radiation over that of undiluted unpolarised blackbody radiation

θ zenith angle, deg

$\cos\theta_0$ cosine of solar zenith angle to the Earth

φ azimuth angle, deg

κ Boltzmann constant, $1.381 \times 10^{-23} \text{ J K}^{-1}$

σ Stefan-Boltzmann constant, $5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$

ν frequency, s^{-1}

Ω solid angle, sr

Ω_0 solar solid angle to the Earth, 67.7×10^{-6} sr

$\chi(\delta_0)$ or $\chi(\varepsilon)$ an asymptotic expression in Eqs. (22), (23) and (24)

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Figure Captions

Figure 1. a) The Earth's TOA LW radiation entropy flux for the Earth's albedo 0.30. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve and dash-dotted curve represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64 and Q_{TOA}/T_P [i.e., $(1 - \alpha_P)Q_0/(4T_P)$], respectively; b) Relative errors to those from Planck's spectral expression.

Figure 2. a) The Earth's net TOA SW radiation entropy flux (the entropy flux from the Earth's reflected TOA SW radiation minus that from incident solar radiation). The solid curve, mark 'o', dashed curve, mark 'x', dotted curve, dash-dotted curve and mark '+' represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64, Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$] and Q_{TOA}/T_{Sun} [i.e., $(1 - \alpha_P)Q_0/(4T_{Sun})$], respectively; b) Differences relative to those from Planck's spectral expression. The thin gray lines in both a) and b) refer to the Earth's albedo 0.30.

Figure 3. a) The Earth's net TOA radiation entropy flux for the Earth's albedo 0.30. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve, dash-dotted curve and mark '+' represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64, Q_{TOA}/T_P [i.e., $(1 - \alpha_P)Q_0/(4T_P)$] and Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$] and Q_{TOA}/T_P and Q_{TOA}/T_{Sun} [i.e., $(1 - \alpha_P)Q_0/(4T_{Sun})$]; b) Relative errors to those from Planck's spectral expression.

Figure 4. a) The Earth's specular reflected TOA SW radiation entropy flux. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve and dash-dotted curve represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64 and Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$] respectively; b) Differences relative to those from Planck's spectral expression. The thin gray lines in both a) and b) refer to the Earth's albedo 0.30.

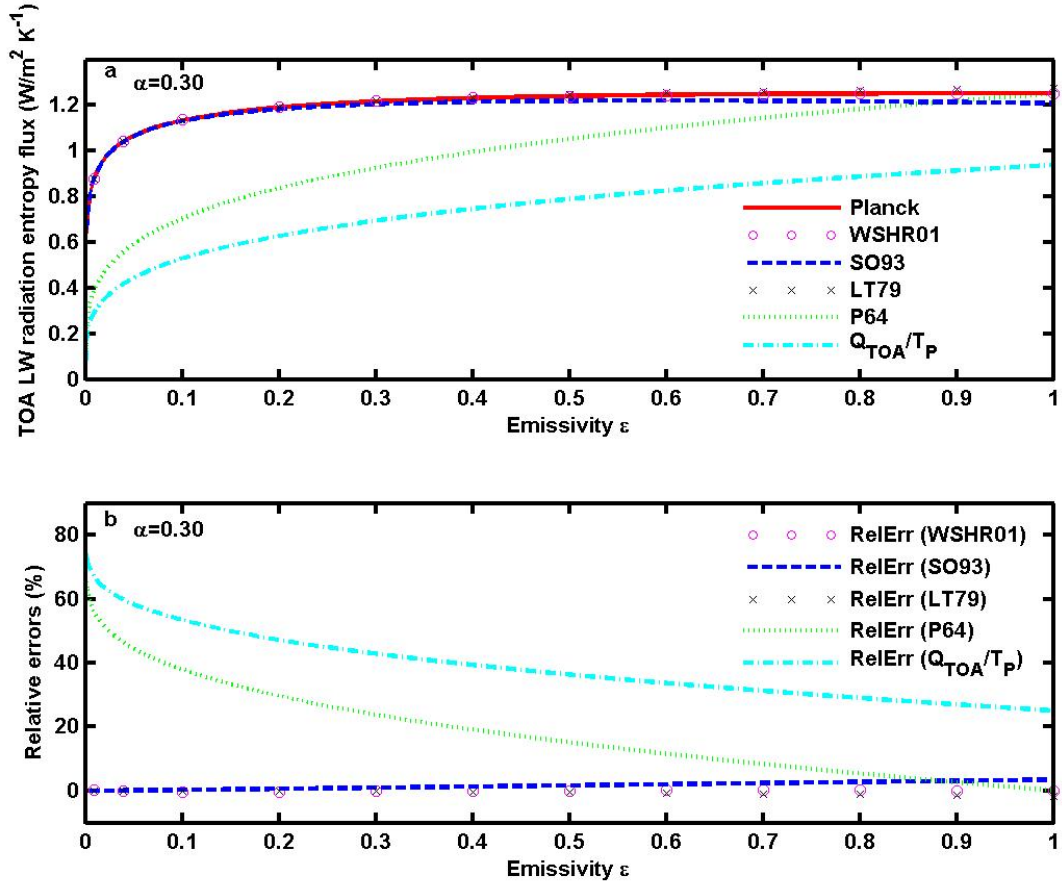


Figure 1. a) The Earth's TOA LW radiation entropy flux for the Earth's albedo 0.30. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve and dash-dotted curve represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64 and Q_{TOA}/T_P [i.e., $(1 - \alpha_p)Q_0/(4T_p)$], respectively; b) Relative errors to those from Planck's spectral expression.

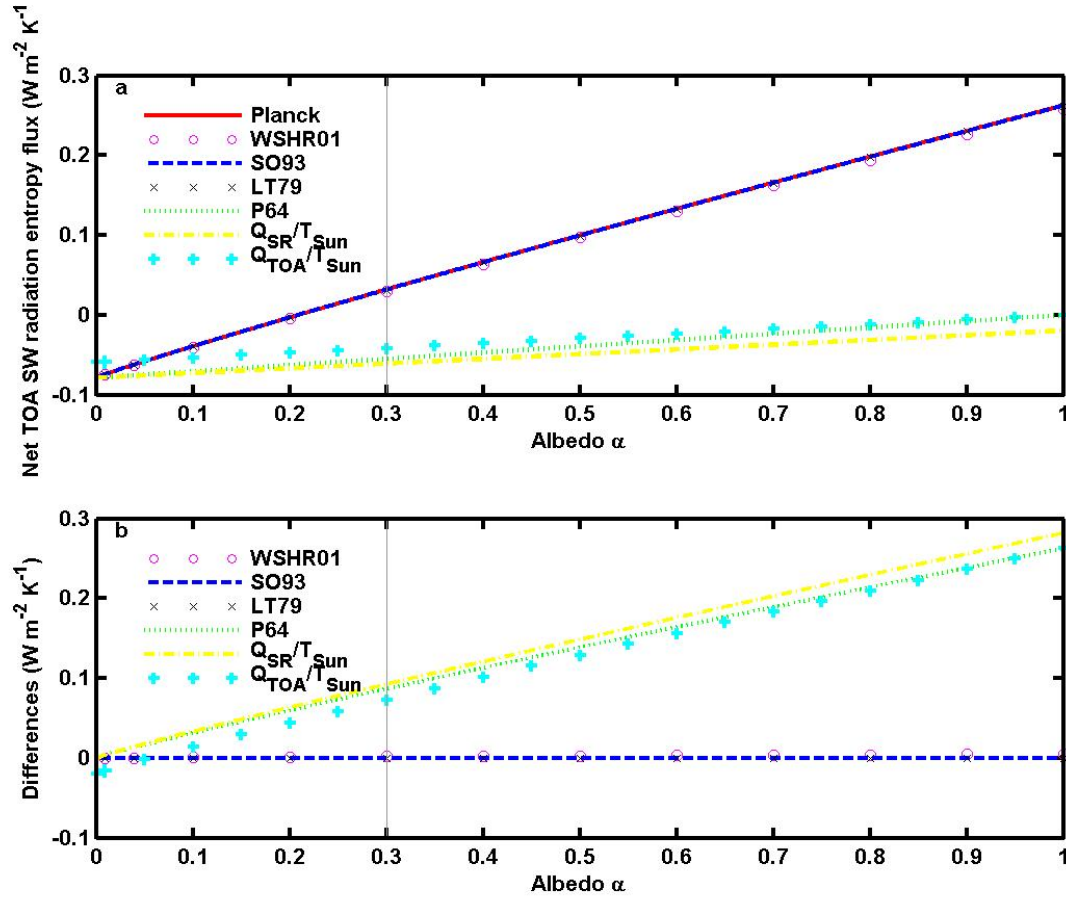


Figure 2. a) The Earth's net TOA SW radiation entropy flux (the entropy flux from the Earth's reflected TOA SW radiation minus that from incident solar radiation). The solid curve, mark 'o', dashed curve, mark 'x', dotted curve, dash-dotted curve and mark '+' represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64, Q_{SR}/T_{Sun} [i.e., $\alpha_p Q_0/(4T_{Sun})$] and Q_{TOA}/T_{Sun} [i.e., $(1 - \alpha_p)Q_0/(4T_{Sun})$], respectively; b) Differences relative to those from Planck's spectral expression. The thin gray lines in both a) and b) refer to the Earth's albedo 0.30.

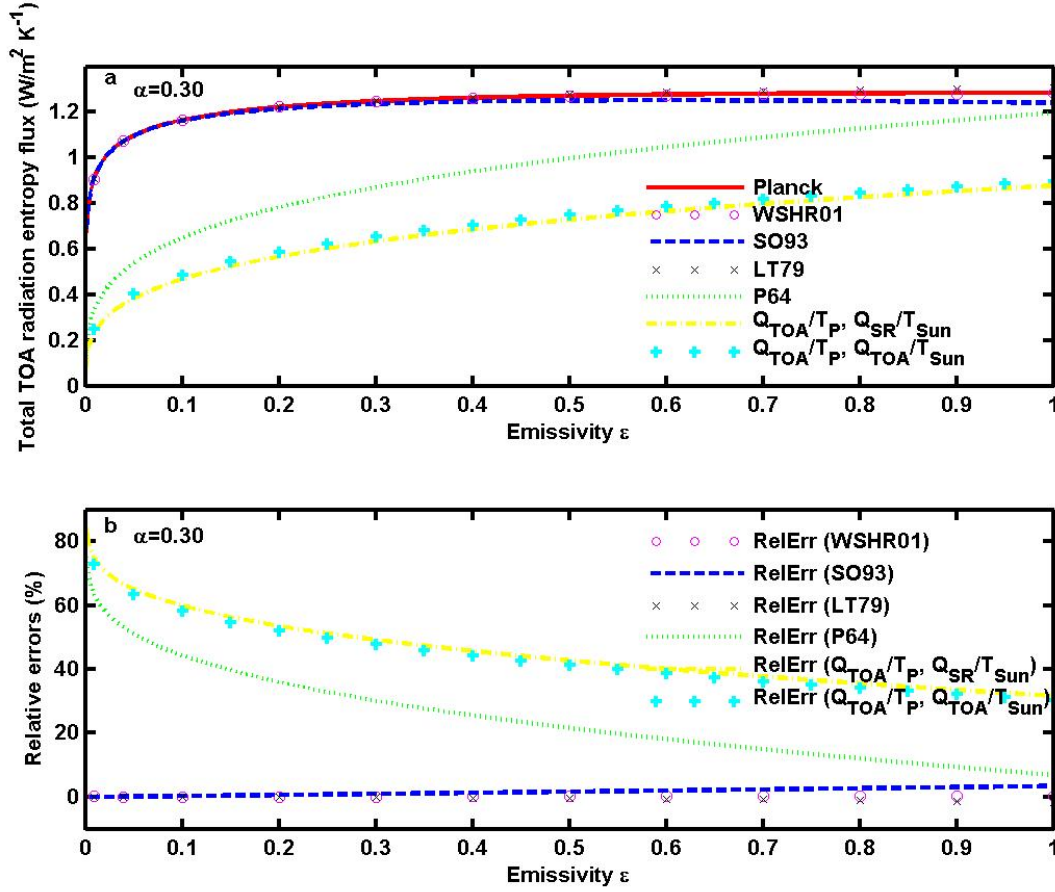


Figure 3. a) The Earth's net TOA radiation entropy flux for the Earth's albedo 0.30. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve, dash-dotted curve and mark '+' represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64, Q_{TOA}/T_P [i.e., $(1 - \alpha_P)Q_0/(4T_P)$] and $Q_{\text{SR}}/T_{\text{Sun}}$ [i.e., $\alpha_P Q_0/(4T_{\text{Sun}})$] and Q_{TOA}/T_P and $Q_{\text{TOA}}/T_{\text{Sun}}$ [i.e., $(1 - \alpha_P)Q_0/(4T_{\text{Sun}})$]; b) Relative errors to those from Planck's spectral expression.

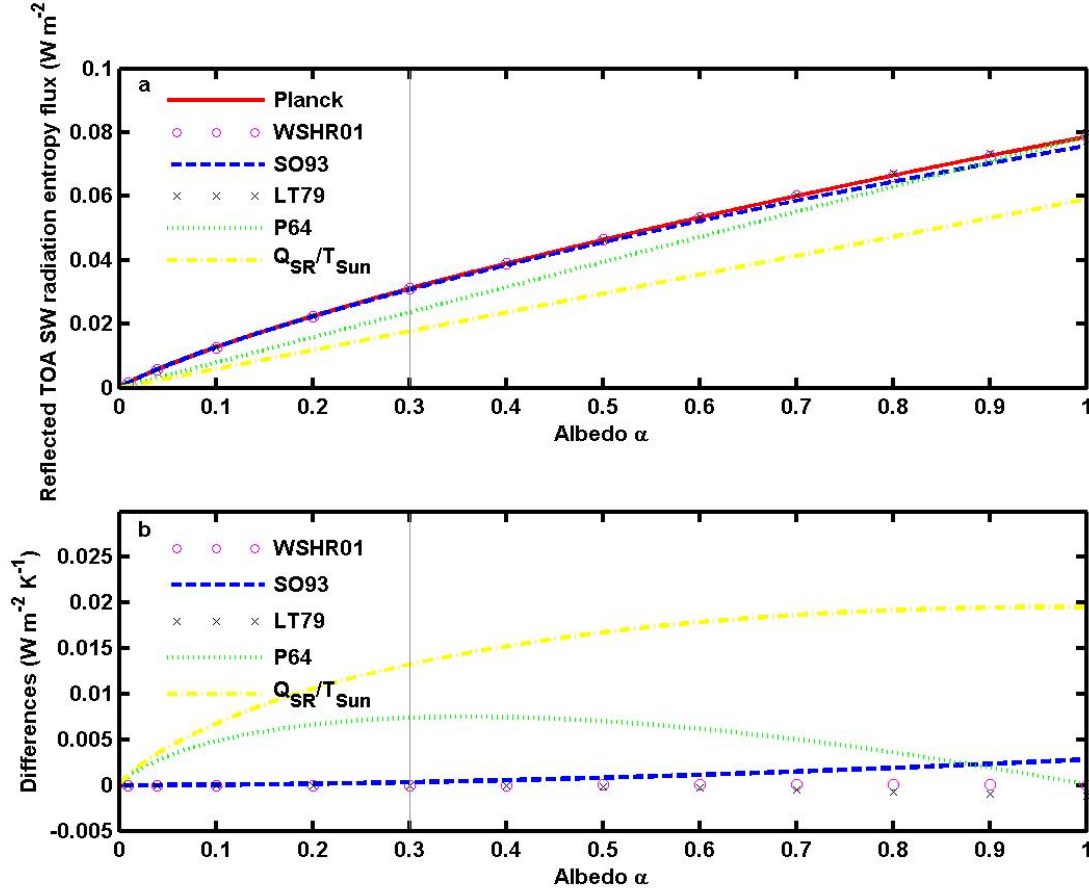


Figure 4. a) The Earth's specular reflected TOA SW radiation entropy flux. The solid curve, mark 'o', dashed curve, mark 'x', dotted curve and dash-dotted curve represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P64 and Q_{SR}/T_{Sun} [i.e., $\alpha_P Q_0/(4T_{Sun})$] respectively; b) Differences relative to those from Planck's spectral expression. The thin gray lines in both a) and b) refer to the Earth's albedo 0.30.